

EP 0185522 B1



Europäisches Patentamt

⑪ European Patent Office

Office européen des brevets

⑪ Publication number:

**0 185 522**

B1

⑪

## EUROPEAN PATENT SPECIFICATION

⑯ Date of publication of patent specification: 07.11.90

⑯ Int. Cl. 5: **C 07 C 69/28, C 07 C 67/08,**  
**C 11 D 3/39**

⑯ Application number: 85309075.1

⑯ Date of filing: 12.12.85

④ Phenylene mixed diester peracid precursors.

⑧ Priority: 14.12.84 US 681983

⑦ Proprietor: The Clorox Company  
1221 Broadway  
Oakland California 94612 (US)

⑥ Date of publication of application:  
25.06.86 Bulletin 86/26

⑦ Inventor: Fong, Ronald Augustus  
513 Avanel Drive  
Modesto California 95356 (US)  
Inventor: Kong, Stephen Bradford  
3318 Washington Court  
Alameda California 94501 (US)

⑥ Publication of the grant of the patent:  
07.11.90 Bulletin 90/45

⑦ Representative: Smith, Sydney et al  
Elkington and Fife Beacon House 113 Kingsway  
London WC2B 6PP (GB)

⑧ Designated Contracting States:  
BE CH DE FR GB IT LI LU NL SE

⑥ References cited:  
"Sauerstoffverbindungen III", pages 547-549,  
Georg Thieme Verlag, Stuttgart, DE  
"Beilsteins Handbuch der Organischen Chemie",  
IV Auflage, Band 6, S. 4416

⑥ References cited:  
EP-A-0 060 092 US-A-3 624 135  
EP-A-0 068 547 US-A-3 624 136  
DE-A-2 038 522 US-A-3 631 227  
FR-A-1 375 960 US-A-3 969 383  
GB-A-1 316 739 US-A-4 036 773  
GB-A-2 073 197 US-A-44 129 34  
US-A-3 462 468

Houben-Weyl: "Methoden der organischen  
Chemie", vol. 8, 4th edition,

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

EP 0 185 522 B1

**Description**

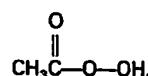
**Field of the Invention**

5 This relates to novel peracid precursors and the in situ generation of peracid in aqueous solution by combining a source of hydrogen peroxide, and the novel peracid precursor which are phenyleno mixed diesters, in water.

**Background of the Invention**

10 Peroxygen bleaching compounds, such as hydrogen peroxide, sodium percarbonate, sodium perborate monohydrate or tetrahydrate, are useful for bleaching fabrics, textiles and other materials. Unfortunately these sorts of peroxygen bleaches appear less effective when bleaching temperatures of less than 70°C are utilized. Thus, the low wash temperature found in American washing machines make the use of these bleaches less effective than in European-type washing machines, which typically use water temperatures above 70°C. Therefore, attempts have been made to use activators in combination with these peroxygen bleaches. It may be more accurate to call these activators peracid precursors, since it is generally accepted that when a molecule of a compound such as sodium acetyloxy benzene sulfonate ("NABS") is combined with a source of hydrogen peroxide, such as sodium perborate monohydrate, in aqueous solution (as indicated in GB 864,798), the result is production of peracetic acid,

20



25 However, nothing within the prior art shows, discloses or suggests that di-substituted benzenes, more specifically, phenyleno diesters, may be appropriate for use as peracid precursors.

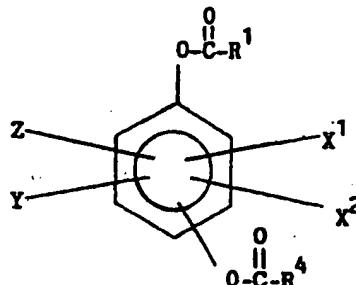
In the description which follows reference is made to US-A-4,412,934 and EP-A-0,068,547. Neither of these documents disclose the use of phenyleno diesters with differing ester moieties.

The invention provides a compound of the general structure:

30

35

40



45

wherein R<sup>1</sup> is alkyl of less than 5 carbon atoms; and X<sup>1</sup>, X<sup>2</sup>, Y and Z are individually selected from H, SO<sub>3</sub><sup>-</sup>, CO<sub>2</sub><sup>-</sup>, NO<sub>2</sub>, NR<sub>4</sub><sup>5+</sup> halogen, R<sup>6</sup> and mixtures thereof;

wherein R<sup>4</sup> of

50

is alkyl of 5 to 11 carbon atoms; R<sup>5</sup> of NR<sub>4</sub><sup>5+</sup> is selected from H, alkyl of 1 to 24 carbon atoms and mixtures thereof; and R<sup>6</sup> is alkyl of 1 to 20 carbon atoms.

The invention also provides a solid or liquid bleaching composition comprising:

(a) A hydrogen peroxide source; and

55

(b) A bleach effective amount of a precursor according to the invention.

Selected adjuncts can be added to these bleaching compositions, such as surfactants, stabilizers, buffers and builders. The invention also includes a method for synthesizing the above noted precursor compounds and a method of bleaching.

60

Washing temperatures of up to 100°C are common in Europe. However, there remains a need to provide peracid precursors which are effective to promote good bleaching in wash temperatures below 70°C, more preferably below 60°C, and most preferably below 50°C.

65

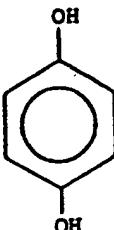
With respect to the ring substituents X<sup>1</sup>, X<sup>2</sup>, Y and Z, in the compounds of the invention which are selected from H, SO<sub>3</sub><sup>-</sup>, CO<sub>2</sub><sup>-</sup>, NO<sub>2</sub>, NR<sub>4</sub><sup>5+</sup>, halogen, R<sup>6</sup> and mixtures thereof (wherein R<sup>5</sup> of NR<sub>4</sub><sup>5+</sup> is selected from H, alkyl of 1-24 carbon atoms, and mixtures thereof and R<sup>6</sup> is alkyl of 1 to 20 carbon atoms), any combination of these substituents may be present in the precursors of this invention. When the

EP 0 185 522 B1

substituents are charged moieties, e.g.  $\text{SO}_3^-$ , appropriate counterpart ions (counterions) may be present. With respect to  $\text{SO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{F}^-$ , appropriate counterions may be chosen from  $\text{H}^+$ , alkali metal salts ( $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{K}^+$ ), although alkaline earth salts (calcium, magnesium, barium) or even ammonium salts may be possible. With respect to a quaternary ammonium substituent, i.e.,  $\text{NR}_3^+$ , appropriate counterions can include halides, ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), methosulfates, sulfates and nitrates. These aforementioned counterions may also be present with respect to the substituted  $\text{R}^1$ ,  $\text{R}^4$  and  $\text{R}^6$  groups, as appropriate.

5 The compounds according to the invention include, ortho, meta and para-substituted phenylene mixed diesters, (i.e. wherein  $\text{R}^1 \neq \text{R}^4$ ) of resorcinol, hydroquinone and catechol, which are exemplified below:

10

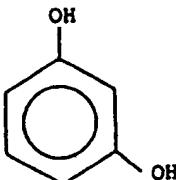


15

20

Hydroquinone (1,4-benzenediol; 1,4-dihydroxybenzene; p-dihydroxybenzene) is a white crystalline compound which can be obtained by dry distillation of quinic acid or by reduction of quinone.

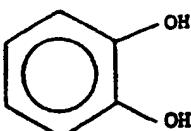
25



30

Resorcinol (1,3-benzenediol; 1,3-dihydroxybenzene; m-dihydroxybenzene) is a crystalline compound with a faint aromatic odor, and a sweet/bitter taste. It may be produced by the alkali fusion of galbanum and asafetida resins.

35



40

Catechol (1,2-benzenediol; 1,2-dihydroxybenzene; o-dihydroxybenzene) is a crystalline compound with a phenolic odor and a sweet and bitter taste. It may be obtained by dried distillation of catechin, which is found in the aqueous extract of catechu, which is an extract of an East Asian acacia plant.

All three of these dihydroxybenzenes starting materials are commercially available.

45

The dihydroxybenzenes are weak acids with two dissociation constants. They are generally classified as antioxidant agents and are useful analytical reagents. Their structures, uses and chemistries are more thoroughly explored in Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd Ed., vol. 13, pages 39-69 (1981), which pages are incorporated herein by reference.

50

The mixed diesterified derivatives of these dihydroxybenzene compounds according to the invention are generally produced by reacting a monoesterified dihydroxybenzene having a group  $\text{O}-\text{C}(\text{O})-\text{R}^1$  or  $\text{O}-\text{C}(\text{O})-\text{R}^4$  with an appropriate acid anhydride providing the other group  $\text{O}-\text{C}(\text{O})-\text{R}^1$  or  $\text{O}-\text{C}(\text{O})-\text{R}^4$  in the presence of a strong acid. The general procedures for making these precursors are set forth below in EXPERIMENTAL.

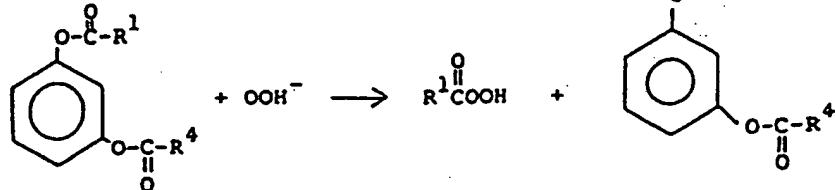
55 It is believed that in situ peracid generation occurs when these novel precursors are combined with a source of hydrogen peroxide in aqueous solution as follows:

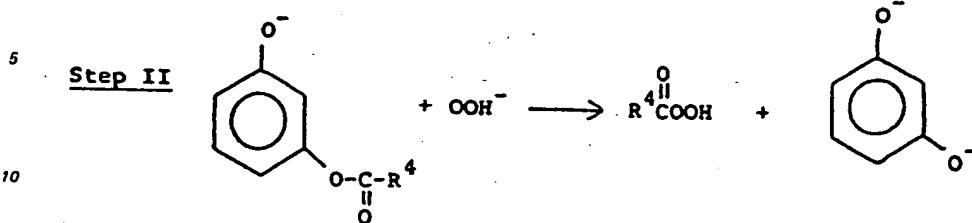
55

60

65

Step I





wherein the phenylene diester precursors revert back to the appropriate dihydroxybenzene compound. While the foregoing is believed to occur, in fact, the mechanism behind peracid generation may occur

15 simultaneously, or in rapid sequence, or a combination of these reactions.

Whatever the mechanism, it was surprisingly discovered that when the novel precursors were combined with hydrogen peroxide in aqueous solution, high yields of peracid were produced, even at low temperatures such as those found in U.S. wash water temperatures. It was even more surprising to see these high yields given that the byproducts of reaction, dihydroxybenzenes, are noted antioxidants which

20 one would expect to consume the peracids thus produced.

Applicants have found these particular substituted phenylene diesters to be particularly effective in low temperature bleaching applications. It was surprising that, given the large number of carbons on the disclosed compositions, the reactivities thereof were suitable for low temperature bleaching applications. Large alkyl groups are hydrophobic, hence solubility or dispersibility in cold water was assumed to be 25 problematic. While enhanced bleaching activity occurs when various solubilizing groups are added to these compositions, sufficient peroxyacid generation for bleach applications has been observed even in their absence.

30 Additionally, applicants observed that with increasing chain lengths of the phenylene diester precursors, decreasing bleaching performance may be observed due to decreasing solubility or dispersibility. Therefore, solubility/dispersibility and hence performance can be improved by the addition of solubilizing groups such as  $\text{SO}_3^-$ ,  $\text{CO}_3^-$ ,  $\text{NR}_3^+$ . Placement of these solubilizing groups may have different effects on the precursor compositions. For example, if the solubilizing groups are placed on the aromatic ring or at or near the end of the alkyl groups of the esters, increased solubility may be observed. Placing the 35 solubilizing groups next to the carbonyl carbon on the ester group or electron withdrawing substituents on the aromatic leaving group may increase the perhydrolysis rate. These theories are by way of explanation and not intended to thereby restrict the invention herein.

35      Addition of the above described substituent groups can be accomplished by ways known to those skilled in the art. For example, halogen groups may be added by typical halogenation reactions, in which a typical source of halogen is combined with the selected dihydroxybenzene starting material in the presence of a Lewis Acid. Nitration, on the other hand, occurs when the dihydroxybenzene is reacted with nitric acid in the presence of sulfuric acid. Sulfonation occurs when the dihydroxybenzene is reacted with concentrated sulfuric acid. On the other hand, amination will generally be produced by reacting a source of amino with the dihydroxybenzene in the presence of liquid ammonia. Further, as with typical benzene-derived compounds, acylation and alkylation can occur via Friedel-Crafts reactions.

40      Especially preferred are solubilizing groups, such as sulfonate ( $-\text{SO}_3^-$ ) or carboxylate ( $-\text{CO}_3^-$ ) groups. These appear to impart good solubility/dispersibility properties to the peracid precursors of this invention. Additionally, it is preferred that a counterpart ion (counterion) to the sulfonate or carbonate group be chosen from  $\text{H}^+$  or an alkali metal ion selected from sodium, potassium or lithium, although alkaline earth counterions and even ammonium counterions may be appropriate.

45      The precursors can be incorporated into a liquid or solid matrix for use in liquid or solid detergent bleaches by dissolving into an appropriate solvent or surfactant or by dispersing onto a substrate material. Examples of appropriate solvents include acetone, non-nucleophilic alcohols, ethers or hydrocarbons. Other more water-dispersible or -miscible solvents may be considered. As an example of affixation to a substrate material, the precursors of the present invention could be incorporated onto a non-particulate substrate such as disclosed in published European Patent Application EP 98 129, whose disclosure is 50 incorporated herein by reference.

55      The phenylene diesters of this invention which contain mixed chain lengths, i.e., a shorter carbon chain length of at least one ester functionality, and a longer carbon length at the second ester functionality, provides extremely proficient bleaching. For example, it is believed that when, according to the invention, one of the ester functionalities has an alkyl straight chain length of less than 5, e.g., wherein  $\text{R}^1$  or  $\text{R}^4$  is  $\text{CH}_3$ , and the other alkyl group's chain length is greater than 5 carbon atoms, peroxyacids which are, respectively, hydrophilic and hydrophobic are generated. The believed advantage thereof is that particulate bleach while oily soils, e.g., sebum, can be attacked with a hydrophilic peroxyacid and hydrophobic soils, e.g., clay soil, and hydrophobic stains, e.g., tea and wine, can be attacked with a hydrophobic peroxyacid. Different pre-formed hydrophobic and hydrophilic peroxyacid bleaches were combined in published European Patent

## EP 0 185 522 B1

Application EP 68 547, whose disclosure is incorporated herein by reference. Pre-formed peracids appear, however, to have storage stability problems and may lose significant amounts of active oxygen (A.O) upon prolonged storage. EP 98 129, mentioned above, discloses in one embodiment, separate peracid precursors which are impregnated on a fabric substrate. Problematic to this approach are the added

5 manufacturing steps to producing different peracid precursors and using slurring, emulsifying or other techniques to bind the different precursors to the substrate. A particularly preferred combination of the present invention is when one ester is an acetate (e.g., R<sup>1</sup> is CH<sub>3</sub>) and the other is an hexanoate, heptanoate, octanoate or nonanoate (e.g., R<sup>4</sup> is -(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub> to -(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>). In a preferred embodiment, the total number of backbone carbons of R<sup>1</sup> plus R<sup>4</sup> should be in the range of 2-20, more preferably 5-20, most

10 preferably 7-14.

Additionally, it was surprisingly found that while the positioning of the ester groups with respect to each other on the phenyl ring is significant, it is not critical. This was surprising since some references had suggested that activators which comprise a substituted phenyl ring must have the active substituent in para configuration with respect to other substituents, likely, it is assumed, to avoid steric hindrance.

15 Under wash conditions and at temperatures below 70°C, it has been surprisingly found that any dihydroxybenzene, whether catechol, hydroquinone or resorcinol, can be used as perhydrolysis leaving groups, and that the resulting antioxidant does not appreciably or rapidly consume the oxidant formed, i.e., the peroxyacid(s). Resorcinol and catechol may be the preferred leaving groups because, of the byproducts of perhydrolysis of ortho, meta and para phenylene diesters, hydroquinone may be the most readily

20 oxidizable.

In the disclosure of Chung, et al., U.S. 4,412,934, it is contended that the molar ratio of hydrogen peroxide to bleach activator must exceed 1.5 or else a competing reaction is favored wherein peracid generated reacts with the bleach activator itself to form diacyl peroxide. In contrast to the Chung, et al. bleach activator, the present invention has been surprisingly discovered to form low levels of diacyl

25 peroxide. This is further depicted below in EXPERIMENTAL, Example II. Although it is not definitely understood why this phenomenon occurs, it appears that the phenylene diester precursors may have different surface active properties. And, because of two reactive sites, which provides two equivalents of peracid per equivalent of precursor, lower concentrations of precursor are needed. There also is no need for a hydrogen peroxide/precursor ratio of greater than 1.5, as mandated in the Chung, et al. disclosure.

30 Based on two reactive sites, i.e., the ester equivalents of the phenylene diester precursors, a ratio of 1:1 hydrogen peroxide:ester is possible, although ratios greater than this are also within the invention. It is preferred that the molar ratio of hydrogen peroxide:ester be from about 1:20 to 20:1, more preferably about 1:10 to 10:1, most preferably about 1:1 to 5:1.

35 While it is explained above that substituting solubilizing groups on the phenyl ring will improve the solubility and enhance the reactivity of these precursors, an alternate mode and preferred embodiment is to combine the precursors with a surfactant. Particularly effective surfactants appear to be nonionic surfactants. Preferred surfactants of use include linear ethoxylated alcohols, such as those sold by Shell Chemical Company under the brand name Neodol. Other suitable nonionic surfactants can include other linear ethoxylated alcohols with an average length of 6 to 16 carbon atoms and averaging about 2 to 20 moles of ethylene oxide per mole of alcohol; linear and branched, primary and secondary ethoxylated, propoxylated alcohols with an average length of about 6 to 16 carbon atoms and averaging 0-10 moles of ethylene oxide and about 1 to 10 moles of propylene oxide per mole of alcohol; linear and branched alkyl-phenoxy (polyethoxy) alcohols, otherwise known as ethoxylated alkylphenols, with an average chain length of 8 to 16 carbon atoms and averaging 1.5 to 30 moles of ethylene oxide per mole of alcohol; and mixtures thereof.

40 Further suitable nonionic surfactants may include polyoxyethylene carboxylic acid esters, fatty acid glycerol esters, fatty acid and ethoxylated fatty acid alkanolamides, certain block copolymers of propylene oxide and ethylene oxide, and block polymers of propylene oxide and ethylene oxide with propoxylated ethylene diamine. Also included are such semi-polar nonionic surfactants like amine oxides, phosphine

45 oxides, sulfoxides, and their ethoxylated derivatives.

Anionic surfactants may also be suitable. Examples of such anionic surfactants may include the ammonium, substituted ammonium (e.g., mono-, di-, and triethanolammonium), alkali metal and alkaline earth metal salts of C<sub>6</sub>-C<sub>20</sub> fatty acids and rosin acids, linear and branched alkyl benzene sulfonates, alkyl sulfates, alkyl ether sulfates, alkane sulfonates, olefin sulfonates, hydroxyalkane sulfonates, fatty acid monoglyceride sulfates, alkyl glyceryl ether sulfates, acyl sarcosinates and acyl N-methyltaurides.

50 Suitable cationic surfactants may include the quaternary ammonium compounds in which typically one of the groups linked to the nitrogen atom is a C<sub>12</sub>-C<sub>18</sub> alkyl group and the other three groups are short chained alkyl groups which may bear inert substituents such as phenyl groups.

55 Further, suitable amphoteric and zwitterionic surfactants which contain an anionic water-solubilizing group, a cationic group and a hydrophobic organic group may include amino carboxylic acids and their salts, amino dicarboxylic acids and their salts, alkylbetaines, alkyl aminopropylbetaines, sulfobetaines, alkyl imidazolinium derivatives, certain quaternary ammonium compounds, certain quaternary phosphonium compounds and certain tertiary sulfonium compounds. Other examples of potentially suitable zwitterionic surfactants can be found described in J. Nes, U.S. 4,005,029, at columns 11-15, which are

65 incorporated herein by reference.

EP 0 185 522 B1

Further examples of anionic, nonionic, cationic and amphoteric surfactants which may be suitable for use in this invention are depicted in Kirk-Othmer, *Encyclopedia of Chemical Technology*, Third Edition, Volume 22, pages 347-387, and McCutcheon's *Detergents and Emulsifiers*, North American Edition, 1983, which are incorporated herein by reference.

5 As mentioned hereinabove, other common detergent adjuncts may be added if a bleach or detergent bleach product is desired. If, for example, a dry bleach composition is desired, the following ranges (weight %) appear practicable:

10	0.5-50.0%	Hydrogen Peroxide Source
	0.05-25.0%	Precursor
	1.0-50.0%	Surfactant
	1.0-50.0%	Buffer
	5.0-99.9%	Filler, stabilizers, dyes, Fragrances, brighteners, etc.

15 The hydrogen peroxide source may be selected from the alkali metal salts of percarbonate, perborate, persilicate and hydrogen peroxide adducts and hydrogen peroxide. Most preferred are sodium percarbonate, sodium perborate mono- and tetrahydrate, and hydrogen peroxide. Other peroxygen sources may be possible, such as monopersulfates and monoperphosphates. In liquid applications, liquid hydrogen peroxide solutions are preferred, but the precursor may need to be kept separate therefrom prior to combination in aqueous solution to prevent premature decomposition.

20 The buffer may be selected from sodium carbonate, sodium bicarbonate, sodium borate, sodium silicate, phosphoric acid salts, and other alkali metal/alkaline earth metal salts known to those skilled in the art. Organic buffers, such as succinates, maleates and acetates may also be suitable for use. It appears 25 preferable to have sufficient buffer to attain an alkaline pH, i.e., above at least about 7.0.

25 The filler material, which, in a detergent bleach application, may actually constitute the major constituent, by weight, of the detergent bleach, is usually sodium sulfate. Sodium chloride is another potential filler. Dyes include anthraquinone and similar blue dyes. Pigments, such as ultramarine blue (UMB), may also be used, and can have a bluing effect by depositing on fabrics washed with a detergent 30 bleach containing UMB. Monastral colorants are also possible for inclusion. Brighteners, such as stilbene, styrene and styrylnaphthalene brighteners (fluorescent whitening agents), may be included. Fragrances used for esthetic purposes are commercially available from Norda, International Flavors and Fragrances and Givaudon. Stabilizers include hydrated salts, such as magnesium sulfate, and boric acid.

35 In another one of the preferred embodiments, in which a mixed diester compound as in (III) above is the precursor, a preferred bleach composition has the following ingredients:

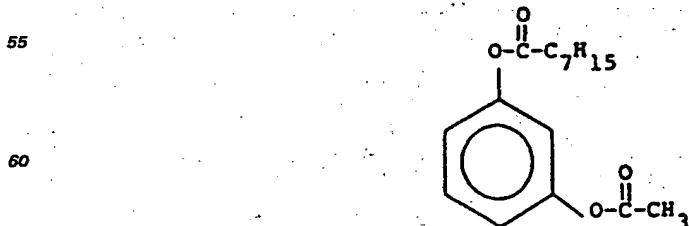
40	15.5%	Sodium Perborate Tetrahydrate
	7.0%	Resorcinol Octanoate Acetate
	7.0%	Nonionic Surfactant
	15.0%	Sodium Carbonate
	55.5%	Sodium Sulfate
	100.0%	

45 The above composition is formulated to deliver, desirably, about 14 ppm A.O. at a pH of about 10.5. Other peroxygen sources, such as sodium perborate monohydrate or sodium percarbonate are suitable. If a more detergent-type product is desired, the amount of filler can be increased and the precursor halved or further decreased.

50 The novel precursors of this invention are synthesized by the methods which are disclosed below. Additionally, performance results are shown below in the EXPERIMENTAL section.

EXPERIMENTAL

I. Synthesis of 1 Octanoyloxy-3-acetoxy benzene



65 An acetoxylated resorcinol is obtained through commercial sources (from American Hoechst). It is placed in a reaction vessel with an equimolar amount of dioctanoic acid anhydride (from Aldrich

## EP 0 185 522 B1

Chemicals), in the presence of methanesulfonic acid to promote acid catalysis, and reacted at room temperature (21°C) for one hour. A 95% yield of the 1 octanoyloxy-3-acetoxy benzene (resorcinol acetate octanoate) and octanoic acid as a by-product results.

In the foregoing synthesis it is believed that any of the dihydroxybenzenes are suitable for use as starting materials. If non-nucleophilic solvents are required, as in base catalysis, acetone (dimethyl ketone), ethyl or methyl acetate, tetrachloromethane, dichloromethane, ethylene chloride, chloroform, and others appear appropriate to the synthesis. The catalyst, 4-dimethylaminopyridine, appears to promote trans-esterification by acting to form a reactive intermediate. Other suitable catalysts may include pyridine and other tertiary aliphatic and aromatic amines. The base, which may act to tie up any carboxylic acid moieties formed in the reaction, may include triethylamine, tetramethyl piperidine,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and suitable tertiary amines. In the selection of suitable bases, care must be taken to insure solubility of the ingredients in the reaction. Similarly, if acid catalysis is the chosen route of synthesis, concentrated sulfuric acid, hydrochloric acid, and methanesulfonic acid are among the catalysts of choice known to those skilled in the art.

15 The purpose of the next experiment was to see if a greater than 1.5 molar ratio of  $\text{H}_2\text{O}_2$ :precursor as contended by U.S. 4,412,934 was actually necessary for the precursors of this invention to give good yields of desired peracids.

### II. Yield of 1 Octanoyloxy-3-Acetoxy Benzene

20 a. The compound synthesized in I (resorcinol acetate octanoate) was combined in aqueous solution with sufficient hydrogen peroxide to yield a hydrogen peroxide:precursor ratio (based on ester equivalents) of about 1.4:1. The reaction conditions were pH 10.5 (based on 0.02M  $\text{NaHCO}_3$ ), temperature 25°C, and 1 g/liter of a nonionic surfactant, Neodol 25-12 (which is a linear ethoxylated alcohol with predominant chain length of 12-15 carbon atoms, averaging about 12 moles of ethylene oxide per mole of alcohol). The concentration of II (resorcinol acetate octanoate) was  $4.375 \times 10^{-4}$  M,  $\text{H}_2\text{O}_2$  was about  $1.225 \times 10^{-3}$  M, to result in an  $\text{H}_2\text{O}_2$ :precursor (based on ester equivalents) ratio of about 1.4:1. Yields of about 75% peracid were obtained. Low levels of diacyl peroxide were detected consistent with the high peracid yield.

25 b. Repeating the above experiment, with the compound of I (resorcinol acetate octanoate) at  $4.375 \times 10^{-4}$  M, but with  $1.75 \times 10^{-3}$  M  $\text{H}_2\text{O}_2$ , to result in a ratio of  $\text{H}_2\text{O}_2$ :precursor of about 2:1, the resulting yield was about 78%. The reason for the absence of substantial diacyl peroxide formation in a competing side reaction as posited by U.S. 4,412,934 are presently unknown. It is speculated that there is a lack of interaction between the recently formed peracid and that portion of unreacted precursor. This theory is for purposes of explanation and not meant to restrict the scope of the invention. It is also believed that any acetyl octanoyl diacyl peroxide formed may be rapidly re-perhydrolyzed, i.e., converted back into peracid, without the need for a large excess of hydrogen peroxide. Further experiments appear to bear out the low diacyl peroxide formation in the inventive compositions.

30 Performance tests for the inventive precursors have also been conducted. The precursors have been found to exhibit significant improvements in bleaching performance over a commercial dry perborate bleach:

### III. % Stain Removal of Crystal Violet/Cotton Swatches of 1 Octanoyloxy-3-Acetoxy Benzene<sup>1</sup>

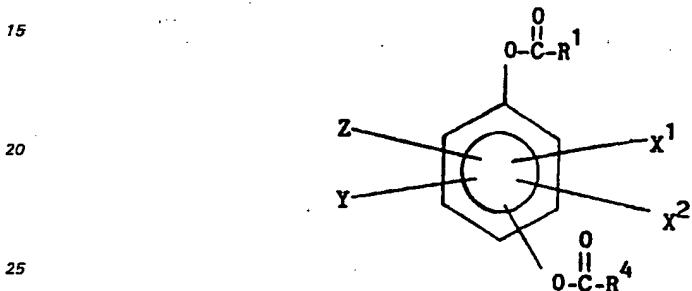
	Composition	% Stain Removal
45	Buffer only	29.7±5.7
	$\text{H}_2\text{O}_2$ + Neodol 25-12	65.8±1.4
50	$\text{C}_2/\text{C}_8$ (7 ppm A.O. theoretical) + $\text{H}_2\text{O}_2$ + Neodol 15-12	76.5±1.5
	$\text{C}_2/\text{C}_8$ (10 ppm A.O. theoretical) + $\text{H}_2\text{O}_2$ + Neodol 25-12	79.0±1.1
55	$\text{C}_2/\text{C}_8$ (14 ppm A.O. theoretical) + $\text{H}_2\text{O}_2$ + Neodol 25-12	82.0±0.4
	Peracetic acid (7 ppm A.O.)	50.4±3.0
60	Peroctanoic acid (7 ppm A.O.)	83.8±1.9
	$\text{H}_2\text{O}_2 = 1.75 \times 10^{-3}$ M pH 10.5 0.02M carbonate buffer 22°C 10 minutes wash time Average of 5 swatches in 200 ml wash water	
65	<sup>1</sup> Resorcinol Acetate Octanoate	

EP 0 185 522 B1

The foregoing description and embodiments of the invention have been presented for purposes of illustration and not intended to restrict the scope of the invention. Other non-limiting embodiments of the invention are possible. For example, standard bleaching and detergent adjuncts may be added to the compositions disclosed. Exemplary of such adjuncts are builders (sodium carbonate, sodium tripolyphosphate, etc.), fillers (e.g., sodium sulfate), brighteners, enzymes (e.g., alkaline proteases), defoaming agents, and the like known to those skilled in the art. Additionally, further esterification of the phenoxy diesters may be possible, for example, resulting in tri- and quaternary-, substituted phenylene precursors. The claims hereto further illustrate the invention.

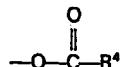
10 **Claims**

1. A compound of the general structure:



wherein R<sup>1</sup> is alkyl of less than 5 carbon atoms; and X<sup>1</sup>, X<sup>2</sup>, Y and Z are individually selected from H, SO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>2</sub>, NR<sup>5+</sup> halogen, R<sup>6</sup> and mixtures thereof;

30 wherein R<sup>4</sup> of



35

is alkyl of 5 to 11 carbon atoms; R<sup>5</sup> of NR<sup>5+</sup> is selected from H, alkyl of 1 to 24 carbon atoms and mixtures thereof; and R<sup>6</sup> is alkyl of 1 to 20 carbon atoms.

40

2. A compound as claimed in claim 1 characterised in that at least one of X<sup>1</sup>, X<sup>2</sup>, Y and Z is halogen selected from the group consisting essentially of Cl<sup>-</sup>, F<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>.

45

3. A compound as claimed in claim 1 characterised in that at least one of X<sup>1</sup>, X<sup>2</sup>, Y and Z are SO<sub>3</sub><sup>-</sup> with a counterpart ion which is H<sup>+</sup> or an alkali metal cation selected from sodium, potassium or lithium.

50

4. A compound as claimed in any of claims 1 to 3 characterised in that O.CO.R<sup>1</sup> and O.CO.R<sup>4</sup> are para in relationship to each other.

55

5. A compound as claimed in any of claims 1 to 3 characterised in that O.CO.R<sup>1</sup> and O.CO.R<sup>4</sup> are ortho in relationship to each other.

6. A compound as claimed in any of claims 1 to 3 characterised in that O.CO.R<sup>1</sup> and O.CO.R<sup>4</sup> are meta in relationship to each other.

60

7. A compound as claimed in claim 1 characterised in that R<sup>1</sup> is CH<sub>3</sub> and R<sup>4</sup> is C<sub>5-11</sub> alkyl.

8. A compound as claimed in claim 7 characterised in that R<sup>4</sup> is C<sub>5-8</sub> alkyl.

9. A bleaching composition comprising:

(a) a source of hydrogen peroxide; and

(b) a bleach effective amount of a peracid precursor which is a compound as defined in any of claims 1 to 8.

10.

10. A composition as claimed in claim 9 characterised in that it further comprises (c) sufficient quantities of buffer to yield an alkaline pH when the composition is placed in aqueous solution.

11.

11. A composition as claimed in claim 9 or claim 10 characterised in that it further comprises (d) a surfactant which will not react with the precursor.

12.

12. A composition as claimed in claim 11 characterised in that the surfactant is selected from anionic, nonionic, zwitterionic, cationic, amphoteric surfactants and mixtures thereof, preferably an anionic surfactant.

13.

13. A composition as claimed in any of claims 9 to 12 characterised in that the hydrogen peroxide source is selected from the alkali metal salts of percarbonate, perborate, persilicate, hydrogen peroxide adducts and hydrogen peroxide.

14.

14. A composition as claimed in claim 13 characterised in that the hydrogen peroxide source is selected from sodium perborate monohydrate or tetrahydrate, sodium percarbonate and hydrogen peroxide.

EP 0 185 522 B1

15. A composition as claimed in claim 13 or claim 14 characterised in that the ratio of hydrogen peroxide yielded by the hydrogen peroxide source to the precursor is greater than 1:1 of hydrogen peroxide to ester equivalent.

5 16. A composition as claimed in any of claims 9 to 15 characterised in that the precursor is selected from phenylene monoacetate monohexanoate; phenylene monoacetate monoheptanoate; phenylene monoacetate monoctanoate; and phenylene monoacetate monononanoate.

17. A method of removing soils from fabrics comprising contacting said fabrics with a bleaching composition as claimed in any of claims 9 to 16.

10 18. A method of producing a bleaching composition comprising combining:

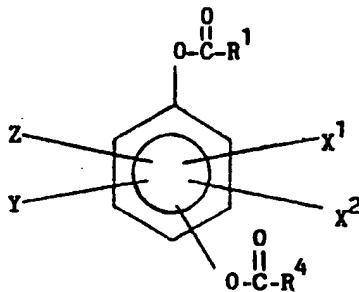
(a) a source of hydrogen peroxide; and

(b) a bleach effective amount of a peracid precursor as claimed in any of claims 1 to 8.

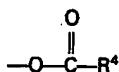
15 19. A method for synthesizing a compound of the formula defined in claim 1 characterised in that one reacts an appropriate dihydroxybenzene selected from the group consisting essentially of hydroquinone, resorcinol and catechol which dihydroxybenzene has been monoesterified to provide a group  $O-C(O)-R^1$  or  $O-C(O)-R^4$  in which  $R^1$  and  $R^4$  are as defined in claim 1 with an approximately equimolar amount of a carboxylic acid anhydride to provide the other group  $O-C(O)-R^1$  or  $O-C(O)-R^4$ .

**Patentansprüche**

20 1. Verbindung der allgemeinen Struktur:



35 worin  $R^1$  Alkyl mit weniger als 5 Kohlenstoffatomen bedeutet und  $X^1$ ,  $X^2$ ,  $Y$  und  $Z$  individuell ausgewählt werden unter H,  $SO_3^-$ ,  $CO_2^-$ ,  $NO_2$ ,  $NR_4^{5+}$ -Halogen,  $R^6$  und ihren Gemischen, worin  $R^4$  von



40 Alkyl mit 5 bis 11 Kohlenstoffatomen bedeutet,  $R^5$  von  $NR_4^{5+}$  ausgewählt wird unter H, Alkyl mit 1 mit 24 Kohlenstoffatomen und ihren Gemischen, und  $R^6$  Alkyl mit 1 bis 20 Kohlenstoffatomen bedeutet.

45 2. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß mindestens einer der Substituenten  $X^1$ ,  $X^2$ ,  $Y$  und  $Z$  Halogen, ausgewählt aus der Gruppe  $Cl^-$ ,  $F^-$ ,  $Br^-$  und  $J^-$ , bedeutet.

50 3. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß mindestens einer der Substituenten  $X^1$ ,  $X^2$ ,  $Y$  und  $Z$   $SO_3^-$  mit einem Gegenion bedeutet, welches  $H^+$  oder ein Alkalimetallkation, ausgewählt unter Natrium, Kalium oder Lithium, ist.

55 4. Verbindung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß  $O.CO.R^1$  und  $O.CO.R^4$  in para-Beziehung zueinander stehen.

5. Verbindung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß  $O.CO.R^1$  und  $O.CO.R^4$  in ortho-Beziehung zueinander stehen.

60 6. Verbindung nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß  $O.CO.R^1$  und  $O.CO.R^4$  in meta-Beziehung zueinander stehen.

7. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß  $R^1$   $CH_3$  und  $R^4$   $C_{5-11}$ -Alkyl bedeuten.

8. Verbindung nach Anspruch 7, dadurch gekennzeichnet, daß  $R^4$   $C_{6-8}$ -Alkyl bedeutet.

9. Bleichzusammensetzung, dadurch gekennzeichnet, daß sie enthält:

65 (a) eine Quelle für Wasserstoffperoxid, und

(b) eine wirksame Menge für das Bleichen aus einer Persäurevorstufe, die eine Verbindung nach einem der Ansprüche 1 bis 8 ist.

10. Zusammensetzung nach Anspruch 9, dadurch gekennzeichnet, daß sie zusätzlich (c) ausreichende Mengen eines Puffers enthält, so daß ein alkalischer pH-Wert erhalten wird, wenn die Zusammensetzung in wässrige Lösung gegeben wird.

## EP 0 185 522 B1

11. Zusammensetzung nach Anspruch 9 oder 10, dadurch gekennzeichnet, daß sie zusätzlich (d) ein oberflächenaktives Mittel enthält, welches mit der Vorstufe nicht reagiert.

12. Zusammensetzung nach Anspruch 11, dadurch gekennzeichnet, daß das oberflächenaktive Mittel ausgewählt wird unter anionischen, nichtionischen, zwitterionischen, kationischen, amphotären oberflächenaktiven Mitteln und ihren Gemischen und bevorzugt ein anionisches oberflächenaktives Mittel ist.

13. Zusammensetzung nach Anspruch 9 bis 12, dadurch gekennzeichnet, daß die Quelle für Wasserstoffperoxid ausgewählt wird aus Alkalimetallsalzen von Percarbonat, Perborat, Persilicat, Wasserstoffperoxidaddukten und Wasserstoffperoxid.

14. Zusammensetzung nach Anspruch 13, dadurch gekennzeichnet, daß die Wasserstoffperoxidquelle ausgewählt wird unter Natriumperboratmonohydrat oder -tetrahydrat, Natriumpercarbonat und Wasserstoffperoxid.

15. Zusammensetzung nach Anspruch 13 oder 14, dadurch gekennzeichnet, daß das Verhältnis von Wasserstoffperoxid, das durch die Wasserstoffperoxidquelle geliefert wird, zu der Vorstufe größer ist als 1:1 Wasserstoffperoxid zu Esteräquivalent.

16. Zusammensetzung nach einem der Ansprüche 9 bis 15, dadurch gekennzeichnet, daß die Vorstufe ausgewählt wird aus Phenylmonoacetatmonohexanoat, Phenylmonoacetatmonoheptanoat, Phenylmonoacetatmonoctanoat und Phenylmonoacetatmonononanoat.

17. Verfahren zur Entfernung von Verunreinigungen aus Textilmaterialien bzw. Flächengebilden, dadurch gekennzeichnet, daß das Textilmaterial bzw. Flächengebilde mit einer Bleichzusammensetzung nach einem der Ansprüche 9 bis 16 behandelt wird.

18. Verfahren zur Herstellung einer Bleichzusammensetzung, dadurch gekennzeichnet, daß (a) eine Quelle für Wasserstoffperoxid, und (b) eine Menge, die zum Bleichen wirksam ist, einer Persäurevorstufe nach einem der Ansprüche 1 bis 8 vermischt werden.

19. Verfahren zur Synthese einer Verbindung der Formel nach Anspruch 1, dadurch gekennzeichnet, daß ein geeignetes Dihydroxybenzol, ausgewählt aus der Gruppe, die im wesentlichen besteht aus Hydrochinon, Resorcin und Catechol, wobei das Dihydroxybenzol unter Bildung der Gruppe  $O-C(O)-R^1$  oder  $O-C(O)-R^4$ , worin  $R^1$  und  $R^4$  die in Anspruch 1 gegebenen Bedeutungen besitzen, monoverestert ist mit der ungefähr äquimolaren Menge eines Carbonsäureanhydrids unter Bildung der anderen Gruppe  $O-C(O)-R^1$  oder  $O-C(O)-R^4$ , umgesetzt wird.

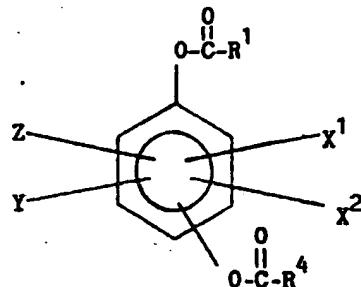
### Revendications

#### 1. Un composé de structure générale:

35

40

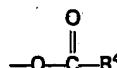
45



dans laquelle  $R^1$  est un alcoyle de moins de 5 atomes de carbone; et  $X^1$ ,  $X^2$ ,  $Y$  et  $Z$  sont individuellement choisis parmi H,  $SO_3^-$ ,  $CO_3^-$ ,  $NO_2$ ,  $NR_4^{5+}$ , un halogène,  $R^6$  et leurs mélanges;

dans laquelle  $R^4$  de

55



est un alcoyle de 5 à 11 atomes de carbone;  $R^5$  de  $NR_4^{5+}$  est choisi parmi H, un alcoyle de 1 à 24 atomes de carbone et leurs mélanges; et  $R^6$  est un alcoyle de 1 à 20 atomes de carbone.

2. Un composé selon la revendication 1, caractérisé en ce qu'au moins un de  $X^1$ ,  $X^2$ ,  $Y$  et  $Z$  est un halogène choisi dans le groupe constitué essentiellement de  $Cl^-$ ,  $F^-$ ,  $Br^-$  et  $I^-$ .

3. Un composé selon la revendication 1, caractérisé en ce qu'au moins un de  $X^1$ ,  $X^2$ ,  $Y$  et  $Z$  est  $SO_3^-$  avec un ion complémentaire qui est  $H^+$  ou un cation de métal alcalin choisi parmi le sodium, le potassium ou le lithium.

4. Un composé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que  $O-CO-R^1$  et  $O-CO-R^4$  sont en relation para l'un par rapport à l'autre.

EP 0 185 522 B1

5. Un composé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que O.CO.R<sup>1</sup> et O.CO.R<sup>4</sup> sont en relation ortho l'un par rapport à l'autre.

6. Un composé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que O.CO.R<sup>1</sup> et O.CO.R<sup>4</sup> sont en relation métal l'un par rapport à l'autre.

5 7. Un composé selon la revendication 1, caractérisé en ce que R<sup>1</sup> est CH<sub>3</sub> et R<sup>4</sup> est un alcoyle en C<sub>6-11</sub>.

8. Un composé selon la revendication 7, caractérisé en ce que R<sup>4</sup> est un alcoyle en C<sub>5-8</sub>.

9. Une composition de blanchiment comprenant:

(a) une source de peroxyde d'hydrogène; et

(b) une quantité blanchissante efficace d'un précurseur de peracide qui est un composé défini dans l'une quelconque des revendications 1 à 8.

10. Une composition selon la revendication 9, caractérisée en ce qu'elle comprend de plus (c) des quantités suffisantes de tampon pour établir un pH alcalin lorsque la composition est mise en solution aqueuse.

11. Une composition selon la revendication 9 ou la revendication 10, caractérisée en ce qu'elle comprend de plus (d) un agent tensio-actif qui ne réagit pas avec le précurseur.

12. Une composition selon la revendication 11, caractérisée en ce que l'agent tensio-actif est choisi parmi les agents tensio-actifs anioniques, non ioniques, zwitterioniques, cationiques, amphotères et leurs mélanges et est de préférence un agent tensio-actif anionique.

13. Une composition selon l'une quelconque des revendications 9 à 12, caractérisée en ce que la source de peroxyde d'hydrogène est choisie parmi les sels de métaux alcalins de percarbonate, de perborate, de persilicate, les produits d'addition de peroxyde d'hydrogène et le peroxyde d'hydrogène.

20 14. Une composition selon la revendication 13, caractérisée en ce que la source de peroxyde d'hydrogène est choisie parmi le perborate de sodium monohydraté et tétrahydraté, le percarbonate de sodium et le peroxyde d'hydrogène.

25 15. Une composition selon la revendication 13 ou la revendication 14, caractérisée en ce que le rapport du peroxyde d'hydrogène fourni par la source de peroxyde d'hydrogène au précurseur est supérieur à 1/1 du peroxyde d'hydrogène à l'équivalent d'ester.

16. Une composition selon l'une quelconque des revendications 9 à 15, caractérisée en ce que le précurseur est choisi parmi le phénylène monoacétate monohexanoate; le phénylène monoacétate monoheptanoate; le phénylène monoacétate monoctanoate; et le phénylène monoacétate monononanoate.

30 17. Un procédé pour éliminer les salissures des tissus comprenant le contact desdits tissus avec une composition blanchissante selon l'une quelconque des revendications 9 à 16.

18. Un procédé pour produire une composition blanchissante comprenant la combinaison de:

35 (a) une source de peroxyde d'hydrogène; et

(b) une quantité blanchissante efficace d'un précurseur de peracide selon l'une quelconque des revendications 1 à 8.

19. Un procédé pour synthétiser un composé répondant à la formule définie dans la revendication 1, caractérisé en ce qu'on fait réagir un dihydroxybenzène approprié, choisi dans le groupe constitué essentiellement par l'hydroquinone, le résorcinol et le pyrocatechol, avec un dihydroxybenzène qui a été mono-estérifié pour fournir un groupe O—C(O)—R<sup>1</sup> ou O—C(O)—R<sup>4</sup> où R<sup>1</sup> et R<sup>4</sup> sont comme défini dans la revendication 1, avec un quantité approximativement équimolaire d'un anhydride d'acide carboxylique pour fournir l'autre groupe O—C(O)—R<sup>1</sup> ou O—C(O)—R<sup>4</sup>.

45

50

55

60

65

THIS PAGE BLANK (USPTO)